STUDY OF SURFACTANTS FOR ENHANCED OIL RECOVERY: DETERMINATION OF INTERFACIAL TENSION AND PHASE BEHAVIOUR OF SELECTED SURFACTANTS

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CERTIFICATION OF APPROVAL

Determination of Interfacial Tension and Phase Behavior of Selected Surfactants for Enhanced Oil Recovery

By

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A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfillment of the requirement for the BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

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UNIVERSITI TEKNOLOGI PETRONAS TRONOH, PERAK MAY 2004

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

The depletion of natural oil resources raises a major challenge to major oil producers in the perseverance of the global economy, in spite of increasing resource consumption and geo-political instability. In order to compensate the challenges faced, there is a need to improve the current oil production techniques and intensify oil production capability.

Applications of engineering and technology are crucial in order to make the attempts possible, and the development of Enhanced Oil Recovery (EOR) techniques is one of study of interest to increase the current oil production efficiency. Chemical EOR is a derivative of the EOR methods and this technique is considered successful as it applies the usage of surfactants in lowering the interfacial tension of the oil and the rock, thus boosts oil production capability. Ergo, physical-chemical properties are the area of interest that is investigated, and extensive experimental works would be the main medium of this study. The properties that are being documented are the determination of the interfacial tension and study of phase behavior of the surfactants that are commonly used in the petroleum industry.

The experimental works are carried out in Petronas Research and Scientific Studies (PRSS), located in Bangi. Spinning drop method is the method used in determination of the interfacial tension, in collaboration with the given equations and correlations. Critical Micelle Concentration is also determined by plotting the surfactant-interfacial tension curve. As for the determination of phase behavior, the method is carried out by simulating the surfactant samples in reservoir temperatures in a specialized oven and it is left by a specified time. The results are collected from respective experiments and analyzed in accordance and viability to the theory.

In overall, experimental works verified the reduction of the interfacial tension and yield desirable phase behavior results. However, there is a need to improve the experimental works and also the fundamental background specifically the physical chemistry mechanics (interfacial tension and phase behavior theory) for the interest of academic research and study.

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CHAPTER 1 INTRODUCTION

1.1 Study Background

Generally, recovery mechanism in an oil reservoir refers to recovery methods applied in order to withdraw hydrocarbons that is trapped within the reservoir. To explain the recovery mechanisms more comprehensively, the fundamentals of an oil reservoir must be fully understood.



Figure 1.01: Illustration of an oil reservoir rock

A reservoir can be defined as subsurface, porous, and permeable rock body in which hydrocarbon (oil and gas) is found. It is confined by impermeable rock and rock barriers that functions to trap the hydrocarbon reserves. A typical reservoir is naturally confined within elevated temperatures and pressures, and this serves as the potential energy mechanism when the reservoir is drilled. It is the ultimate interest for the oil to be recovered, and basically the recovery mechanisms that are used are primary or natural methods, secondary methods, and tertiary or enhanced oil recovery methods. These recovery mechanisms can be referred in the following diagram:



Natural drive mechanisms apply potential energies that are contained within the reservoir due to elevated temperatures and pressures. A typical reservoir condition is initially within the pressure of 4000 psia and temperature of 200°F. When a production well is drilled to the reservoir, these natural energies would drive the oil to the production tube. However, the pressure within the reservoir would drop with respect to time, and eventually results slower recovery rate. At this point, the recovery rate with respect to

the oil originally in place (OOIP) is only 15-30% (Elsevier, 1981). Therefore, secondary drive mechanism is applied with the objective to sustain the pressure drop within the reservoir and eventually increases the oil recovery. Nevertheless, production statistics showed that secondary drive mechanism would only recover up to 60% of oil recovery.



Figure 1.03: Natural Drive Mechanism and Relation to the Oil Recovery Rate to OOIP

With approximately 60% OOIP abandoned in reservoir using conventional recovery mechanisms (primary and secondary), the challenge in the petroleum industry is to maximize recover the residual oil trapped inside the reservoir. This challenge is also driven by other factors. These factors would also include:

- Increasing fuel consumption demand for energy source;
- Decreasing oil reserves in major oil wells;
- Increasing political instability at Mid-East Asia;
- Increasing difficulty of oil exploration and its costs;
- Challenge of cost cutting methods in exploration and production.

Technically, the factors of the unrecoverable oil within the reservoir is due to poor mobility control or arising from heterogeneity, or is trapped by capillary forces, as a result from the high interfacial tension between the reservoir crude oil and water. Realizing the challenges and constraints faced, EOR remained the main interest to improve the oil recovery up to its maximum capability. Chemical Flooding is one of the effective methods used for EOR. It applies the usage of surfactants, in which of its capability to reduce the interfacial tension between the oil and water. In contrast to other EOR methods, Chemical EOR (CEOR) processes are applicable to a wide range of reservoir conditions, with small dependence of temperature and pressure property changes. Engineering economy analysis verifies that applying CEOR is economically feasible from Present Worth (PW) and Annual Worth (AW) Methods, due to its ability to oil reserve addition and extending the field life (Surtek, 2003).

Surfactants are primarily used in CEOR and it is normally associated with polymer to function as the mobility control. Apparently, surfactants are not only applied in CEOR methods, but to other industrial applications as well, especially in producing detergents, household cleaning products, and hygiene care products. This can be explained by its unique molecular structure and characteristics, which involves hydrophilic and hydrophobic properties. In its role for EOR, the usage of surfactants is essential in order to reduce the IFT, and ability to alter the physico-chemical properties between the oil and the water within the reservoir. This explains why the physico-chemical properties are the main focus in evaluating and analyzing surfactants. Such properties that are studied are IFT, Critical Micelle Concentration (CMC), Phase Behavior, Kraft Point, Cloud Point, and Adsorption Level.

For this research, the parameters of interests are the determination of IFT and Phase Behaviors of the selected surfactants that is to be applied in CEOR. These parameters are to be determined experimentally, using available laboratory design methods.

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1.2 Problem Statement

The determination of IFT and Phase Behavior of the selected surfactants requires an extensive fundamentals study of surfactants and EOR in order to give a better insight and better understanding approach of its physico-chemical properties. In addition, the experimental results of the IFT and Phase Behavior would give credible information to analyze the ideal specifications and requirements of surfactants for Enhanced Oil Recovery.

1.3 Objectives and Scope of Study

The main objectives of this study are:

- 1.3.1 To study basic principles of Enhanced Oil Recovery (EOR) and the role of Surfactants, mainly to its physico-chemical properties and its importance in chemical flooding.
- 1.3.2 To determine IFT and Phase Behaviors for selected surfactants that is to be used via experimental works in Petronas Research Scientific Studies, PRSS.

The scope of this study are to experimentally determine the IFT values of surfactants in different concentration compositions, and phase behavior whilst identifying the ideal specifications and requirements for it to be applied in chemical flooding. A comparison and discussion of experiment results based on theory being conducted in collaboration of Petroleum Engineers, EOR Chemists, lecturers so strengthen the research credibility. Results from other case studies are also taken as a part of reference to the research study.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Surfactants – A General Overview

Surfactant is contraction of the term "surface active agent," which generally describes their primary attribute. These chemicals tend to spontaneously concentrate at the interface or "surface" between immiscible fluids or between a fluid and solid due to their unique chemical structure. The surfactant molecule will have a portion that is attracted to one fluid or solid phase which termed as lyophilic, and another portion that repels the phase (lyophobic). An example of a surfactant molecule is shown in the following diagram:



Figure 2.01: Alkyl-Aryl Sulfonate



Figure 2.02: A surfactant chemical sample

As explained initially, the molecule of a surfactant comprises of hydrophilic and hydrophobic structure. The jargon hydrophilic can be referred as the "head" and deemed as water loving portion that contains polar and ionic characteristics that would readily dissolve in water. Meanwhile, the hydrophobic structure is referred as the tail of the surfactant, in which they will repel water. These types of structure causes the molecules to orient themselves so that the lyophilic structure is within the solvent and the lyophobic structure is away from it, thus concentrating at an interface.



Figure 2.03: Surfactant in oil-water system

When a surfactant is dissolved in oil, the solvent molecules in the bulk solution (oil and water) interact within similar molecules within the solvent, but at the interface, they interact with dissimilar molecules, causing those at the surface to have higher potential energy. The surfactant molecules at the interface reduce this force imbalance or surface tension. Consequently, as the surfactant molecules concentrate at the interface, longer work is required to move a molecule of solvent from the bulk solution to the interface than for moving a surfactant molecule. The surfactants then increase the free energy of the system, or referred as the Gibbs free energy. The association of free energy with the interfacial phenomena is advantageous because the total free energy change can be attributed to the sum of contributions of free energy change by individual molecular structural groups.

2.2 Types of Surfactants

There are four main classes of surfactants available, and they are:

- Anionic
- Cationic
- Nonionic
- Zwitterionic

The types of surfactants are distinguished upon the nature of the hydrophilic group, which is the molecular structure. In addition, these classes of surfactants have their own respective industrial applications due to its specific hydrophilic properties. As such, the first two are ionic species in aqueous solution that carry, respectively, a negative and positive charge. In contrast with hydrophobic structure, this is less pronounced.

Most solid surfaces are negatively charged, including reservoir rock. Cationic surfactants are attracted to the negative charge; so much of their application is related to adsorption to solid substrates. They are used as floatation agents, anti-static agents, fabric softeners, pigment dispersants, corrosion inhibitors, etc. Because of their high adsorption, they are not practical for chemical enhanced oil recovery.

Non-ionic surfactants are brine tolerant, compatible with other classes of surfactants, hard water tolerant. The disadvantage of non-ionics is that they are liquids or pastes, more expensive than anionics, and less soluble at higher temperatures.

Anionic surfactants are the mostly applied chemical type in chemical enhanced oil recovery. This class in itself contains a very wide range in molecular structure and functional groups, and therefore a wide range of properties can be identified. Anionic surfactants as a class are the least adsorbed onto common negatively charged solid surfaces like reservoir rock, which has the advantage in CEOR that it minimizes adsorption losses. Certain types of anionic surfactant can be manufactured relatively and inexpensively, and this explains it is economically feasible for it to be applied in chemical flooding.

2.3 Role of Surfactants, Polymer, and Water in Chemical Flooding

As explained before, the role of surfactant is crucial in chemical flooding since it lowers the interfacial tension between the oil and the water. Reduced interfacial tension propagates the oil, and the driving fluid which is the polymer would drive the solubized oil to the production tube. Thus, it can be said that the role of surfactants in chemical flooding is in collaboration with other chemicals, primarily polymers and drive water. The ultimate function of the polymer is to provide mobility control to the surfactant during the chemical flooding. In detail, the polymers are used to increase solution viscosity, flocculate fines, to break emulsions, and to plug high permeability zones of a reservoir. This prevents any immobilization and trapping that will consequently lead to surfactant losses, and avoiding any economic losses for chemical flooding.



Figure 2.04: Chemical Flooding Process

Figure 3.04 shows a representation of a chemical flooding process using water, polymer and surfactant. The waterflood residual oil saturation near the production well is on the order of 40% and only water is being produced. A series of "slugs" were injected, shown as surfactant, polymer, and water that have reduced the oil saturation, and thereby developed a "bank" of oil. When this bank reaches the production well, oil will be produced with the water at increased oil cut. If the total fluid production rate remains unchanged, the increase in oil cut is proportional to the increase of oil production rate.

2.4 Physical Properties of Surfactants: CMC, IFT, and Phase Behavior

Explicitly, the properties of surfactants that are analyzed for EOR are the Critical Micelle Concentration, Kraft Point, Conductivity, Viscosity, Adsorption Level, and Interfacial and Surface Tension at the Critical Micelle Concentration.



Figure 2.05: Illustration of the physical property changes due to presence of surfactants

Critical Micelle Concentration or CMC is defined as the critical concentration whereby the molecular aggregates termed micelles are formed (Schramm, 2000). The cmc is a property of the surfactant. Significance of cmc can be explained the concept of micellar parameters. Formation of micelles is due to the formation of organized aggregates of large numbers of molecules, where lipophilic parts of the surfactants associate in the interior of the aggregate leaving hydrophilic parts to face the aqueous medium. CMC is one of the most important parameters because at concentrations above this value the adsorption of the surfactant onto reservoir surfaces increases very little. It represents the solution concentration of surfactant from which nearly maximum adsorption occurs.

Krafft point T_k is defined as the solubilities of micelle-forming surfactants above a certain temperature (Schramm, 2000). At T_k , a relatively large of amount of surfactant can be dispersed in micelles and solubility increases greatly. Above the Krafft point maximum reduction of IFT occurs at the cmc because the cmc then determines the surfactant concentration.

Surface tension is can be visualized by the contracting force at the surface, and it is due to the attractive van der Waals forces between molecules are felt equally by all molecules except those in the interfacial region this imbalance pulls the latter molecules towards the interior of the liquid. Surface tension is an important parameter because it displays the surface energy required for the foam formation to occur. It is desired for a surfactant to lower the surface tension as it would lead to lowering of the IFT, and at the same time less mechanical energy required for the formation of foam to occur within the oil. This is done by the expanding force acting against the normal interfacial tension. Interfacial tension is normally represented in terms of dynes/cm. Before the surfactant is injected within the reservoir, the normal IFT between the oil and rock is at 20 dynes/cm(Schramm, 2000). This is considered a large value because it results the

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binding of the oil and the water, making it trapped between the reservoir rock, and consequently, limits the oil recovery capability. Introducing surfactants will tamper the normal interfacial tension of the oil and water, due to its interaction and propagation of oil, the surfactant reduces the IFT to the range of 0.002 dynes/cm (Schramm, 2000). At this range, this makes the oil recovery highly desirable, and surfactants is the main chemical component in chemical flooding. There are lot of equations and methods in order to calculate the IFT, and generally it is a function of capillary pressure, adhesive forces between the oil and rock, and adhesion tension between oil-water and oil rock. Spinning drop method is usually applied in determining the IFT of the surfactants, and followed by the equation:

IFT = (Spinning Drop Constant) (Speed (ms/rev))⁻² ($R_2 - R_1$)³ ($\rho_s - \rho_c$)

Where the

 R_1 = Primary distance of elongated oil droplet

 R_2 = Secondary distance of elongated oil droplet

 ρ_s = density of solution, (g/cm³)

 ρ_c = density of crude oil, (g/cm³)

Phase Behavior in surfactant property evaluation is normally represented by phase diagrams. These diagrams is used to explain the behavior of surfactant systems. A typical diagram that is used is ternary phase diagram, which associates three different components, which are surfactant, brine and oil. In reservoir ternary diagrams, the components represented no longer true portray true thermodynamic components since they are in mixture forms. A crude oil contains hundreds of components, and the brine and surfactant pseudocomponents may also be complex mixtures. The ternary diagram shows the best representation of the phase behavior and it is reasonably accurate as long as each component has approximately the same composition in each phase. In evaluating phase diagrams, phase behavior type descriptions are used. Usually, it is classified

according to physical observation of the mixture and crude oil. The classification of phase types are tabulated in the following:

Phase Type	Phase Type Description
П	Two fluid envelopes exist - a bottom aqueous phase and top oil
	phase. Color is not visible in the aqueous phase. The crude oil and
	aqueous phase are equal to the volumes placed in the tube. No crude
	oil swelling has taken place.
II-	Two fluid envelopes exist, which comprises of bottom aqueous phase
	and an oil phase. The bottom aqueous phase is colored indicating the
	alkali has saponified acids in the crude oil which is present in the
	aqueous phase.
Ш	Three or more fluid envelopes exist, which comprises of bottom
	aqueous phase, middle emulsion phases, and top crude oil phase.
<u>II</u> +	Two fluids envelopes exist, where a bottom aqueous phase and a top
	crude oil phase are present. The bottom aqueous phase is clear
	because the surfactant reside in the crude oil phase.

Table 2.01: Surface Phase Types Description

According to table 2.01, type III is the desired phase type to recover additional oil followed by type II-, II+ and type II. This is explained by the presence of interaction between the aqueous phase, crude oil and saponified acids. The relation to ternary phase diagrams explains the equilibrium interaction between of the three major components. Type II- phase behavior refers to the lowest salinity or lowest brine content in the solution. This is because most of the brine water is dissolved in the surfactant, interpreting that the surfactant is water soluble. Should the salinity increases, the surfactant would be more oil soluble, making the phase behavior to be in the type III

region, where the phases are distinguished by the top oil phase, middle emulsion phase, and bottom aqueous phase. Increasing the salinity changes the phase behavior, and transforming the solution to be in the region of type II+. Here, it can be concluded that the surfactant is oil soluble, where most oil is dissolved in surfactant and in form of microemulsion followed by brine water. From the phase behavior explanations, type III verifies as the most desired phase behavior that the evaluations trying to achieve because it shows balanced interaction with the brine and the oil. It is also the target characteristics within the chemical flooding, where the main target is to minimize surfactant losses, and minimize oil solubility to the surfactant so that separation between the oil and the surfactant is easier and economically feasible.



Figure 2.06: Ternary Phase Diagrams on Evaluating Phase Behavior of Surfactants

For surfactant adsorption in porous media, this phenomenon can be described as the electrostatic interaction, van der Waals interaction, hydrogen bonding and salvation and desolvation of adsorbate and adsorbant species. Normally it is a common effect for the surfactant to be adsorbed onto solid surfaces specifically to the porous media, either on the walls of pores or fine particles in rock pores. In EOR, adsorption constitutes a loss of valuable surfactant and it is directly affects the economic success of the flooding process.

Thus, adsorption study is considered important so that the factors that influence adsorption and its consequences can be identified and acknowledged. From there, preventive measures by altering the properties or introduce inhibition of the surfactant could be done to minimize adsorption on the porous rocks, while maintaining its recovery efficiency. Through analysis, factors that influence adsorption are temperature, brine salinity and hardness, solution pH, rock type, wettability, and the presence of a residual oil phase.

2.4 Laboratory Design Scale of Determining IFT and Phase Behavior

The determination of Interfacial Tension and Phase Behavior is done with respective to stages, using appropriate tools and equipments. These are done experimentally, and normally are done repeatedly in order to improve results consistency and accuracy. The works are done as follows:

- Preparation of Surfactant Solutions
- Preparation of Surfactant Solutions respective to brine and connate water composition
- Screening tests for Surfactant Samples
- Spinning Drop Method for determination of IFT
- Determination of Phase Behavior

Generally, the experimental works is defined as the fluid-fluid evaluation scale and this is where the physical properties of the surfactants is determined. However, at this stage, the results is still considered as preliminary and fluid-rock evaluation activities is carried out to further evaluate the surfactants in more detail, through the experimental tests in collaboration with the reservoir rock and polymers. For the relevance of this research, three fluid-fluid evaluation experiments are conducted to satisfy the project objectives.

CHAPTER 3 METHODOLOGY

3.1 Research Procedures Identification

For the detail study conducted, several procedures are identified and structured into several key points;

3.1.1 Preliminary Literature Review and Data Gathering

- All books describing Surfactants and Enhanced Oil Recovery are gathered by continuous retrieval from information resource center.
- Websites and online information involving surfactants are also gathered via internet. Journals and case studies are also gathered by this media; however most of the information is collected from the resource center.
- Information gathered are rearranged and revised in accordance to the relevance of the project. All information that is gathered is discussed with the selected supervisor.

3.1.2 Experimental Work Setup and Execution

After conducting literature review, an arrangement is made with the Senior EOR Chemist at Petroleum Research Scientific Services (PRSS), Bangi, to discuss the available experiments that can be conducted involving Surfactants for EOR. Based on the meeting, it was agreed upon that three experiments can be done involving surfactant study, which are:

- Preparation and Density Determination of Surfactant Samples $\sqrt{1}$
- IFT Determination ✓
- Phase Behavior Investigation Experiment

Allocation of the experimental works is set-up within the duration of one month, with 2 day sessions once in every week.

3.1.3 Results Gathering and Data Analysis

After the result of the experiments is obtained, discussion with the EOR Chemist, Petroleum Engineer, and EOR technician are done in collaboration for interpretation and analysis. The results are tabulated and illustrated in graphical forms to display relationships with one parameter variable to another. Most of the results gathered are compared relatively to the governing theory, and at the same time recommendations are proposed in order to improve the experimental works and results. A discussion with the UTP lecturers is also done in order to strengthen the results, making the research project more credible.

3.1.4 Preparation of Report

The preparation of report is prepared in accordance with the research and course requirements. Subsequently, the report serves as a future reference of study for further research development.

3.2 Experimental Equipments

For the experiments conducted, several equipments are required in order to process the surfactant samples. These equipments are available at PRSS, and for this research, two equipments would be used. A simple briefing of the required equipments is necessary in order to provide useful information in terms of handling and safety procedures. The equipments involved in the experiments are:

- IFT Experiment: Spinning Drop Tensiometer 🗸
- Phase Behavior Experiment: Oven

3.2.1 Spinning Drop Tensiometer

The Spinning Drop Tensiometer is used to calculate the elongated oil droplet after it is being centrifuged to a certain revolution and elevated temperature. It comprises of several parts, and it can be viewed by the following figure:



Figure 3.01: Spinning Drop Tensiometer V

In detail, the spinning drop equipment is a UT Model 500 leased from Surtek, Inc. However, further technical specifications for this equipment are unavailable due to the confidentiality of the supplier. Nevertheless, this equipment is generally simple and its parts are easy to use and their function can be easily utilized.

3.2.2 Oven

Oven is used in order to provide elevated temperature conditions for the surfactants at elongated time. However, the desired heating conditions would be at elevated temperature and pressure conditions, so that the reservoir simulation environment is more accurate, and the conditions applied on the surfactant samples are more definite. For the oven used in this experiment, the only parameter used is the temperature, and to simulate reservoir conditions, a temperature setting of 90° C is keyed in. The oven known supplied by Memmert, Inc. The oven can be viewed in the following figure:



Figure 3.02: Oven

3.3 Chemicals Used

Three types of chemicals are used for this research, and they are:

- Surfactants
- Polymer
- Brine Water (Obtained from production well)
- Connate Water (Obtained from production well)
- Seawater (Prepared by PRSS)
- Crude oil

Perhaps the most important chemical used are the surfactants and polymers, and it is supplied from various manufacturers. These surfactants and polymers can be referred at Table 3.01.

Manufacturer	Туре	Product Name
		1

Stepan	Surfactant	Agent 2385-81A
		Agent 2385-81B
Oil Chem. Technologies V	Surfactant	Sample no. 6-82
	۲	Sample no. 6-79
		Sample no. 6-77
Crompton	Surfactant	Petronate EOR-2095
Cytec	Polymer 🗸	Superfloc BD319

Table 3.01: List of Surfactant and Polymers used

However, the complete chemical name of the supplied surfactants polymers could not be obtained due to confidential reasons by the supplier. Nevertheless, based on theoretical review, it can be verified that the type of surfactants used for EOR is anionic type.

3.2 Experimental Procedures

3.2.1 Preparation, Density Determination, and Evaluation of Surfactant Samples

I.



Solution	Quantity		n della significa Nationalista	S	urfac	ant @ concentration	on		
SUBLICH	ml	0.05%		0.10%		0.15%		0.20%	
А	100	0.12 ml	A1	0.23 ml	A2	0.35 ml	A3	0.47 ml	A4
В	100	0.12 ml	B 1	0.23 ml	B2	0.35 ml	В3	0.47 ml	B4

с	100	0.12 ml	C1	0.23 ml	C2	0.35 ml	Сз	0.47 ml	C4
D	100	0.12 ml	D1	0.23 ml	D2	0.35 ml	D3	0.47 ml	D4
Е	100	0.12 ml	E1	0.23 ml	E2	0.35 ml	E3	0.47 ml	E4

Table 3.01: Prepara	ation of Sur	factant Samples
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3.2.2 Determination of Interfacial Tension (IFT) of Selected Surfactants

3.2.3 Determination of Phase Behavior

Injection Water	Produced Water	Phase Behavior at Surfactant Concentration of							
0	100	0.05%	0.10%	0.15%	0.20%				
25	75								
50	50								
75	25								
100	0								

Table 3.02: Results table for Phase Behavior of different Surfactant Concentrations

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Preparation, Density Determination, and Evaluation of Surfactant Samples

Referring the experimental procedures conducted, the results are tabulated in Table 4.01 and Table 4.02. Table 4.01 refers to the quantity of surfactant injected to the samples in terms of concentration.

Surfactant

: Sample No. 6-79 Polymer : Superfloc BD319

Colution	Quantity			Surfactar	it @ c	oncentration			
Solution	ml	0.05%	1 malai	0.10%		0.15%		0.20%	5465×6
Α	100	0.12 ml	A1	0.23 ml	A2	0.35 ml	A3	0.47 ml	A4
В	100	0.12 ml	B1	0.23 ml	B2	0.35 ml	B3	0.47 ml	B4
С	100	0.12 ml	C1	0.23 ml	C2	0.35 ml	C3	0.47 ml] C4
D	100	0.12 ml	D1	0.23 ml	D2	0.35 ml	D3	0.47 ml	D4
E	100	0.12 ml	E1	0.23 ml	E2	0.35 ml	E3	0.47 ml	E4

Table 4.01: Preparation of Surfactant (Sample No. 6-79) Samples with respect tosurfactant concentration, injection and produced water

Surfactant

: Sample No. 6-66 Polymer : Superfloc BD319

Colution	Quantity			Surfacta	nt @ c	oncentration	i prasi e		
Solution	ml	0.05%		0.10%		0.15%		0.20%	
Α	100	0.12 ml	A1	0.23 ml	A2	0.35 ml	A3	0.47 ml	A4
В	100	0.12 ml	B1	0.23 ml	B2	0.35 ml	B3	0.47 ml	B4
C .	100	0.12 ml	C1	0.23 ml	C2	0.35 ml	C3	0.47 ml	C4
D	100	0.12 ml	D1	0.23 ml	D2	0.35 ml	D3	0.47 ml	D4
E	100	0.12 ml	E1	0.23 ml	E2	0.35 ml	E3	0.47 ml	E4

Table 4.02: Preparation of Surfactant (Sample No. 6-66) Samples with respect tosurfactant concentration, injection and produced water

According to the procedures, to evaluate the samples prepared, 5mL of solution is mixed with 5mL of crude oil and is left in the oven with the temperature setting of 90°C in one week. Evaluation results are gathered in Table 4.03 and Table 4.04.

Surfactant

: Sample No. 6-79 Polymer : Superfloc BD319

Colution	Quantity	y Surfactant @ concentration								
Solution	mi	0.05%	140.12	0.10%		0.15%		0.20%	la anna	
Α	100	Clear	A1	Clear	A2	Clear	A3	Clear	A4	
В	100	Clear	B1	Clear	B2	Clear	B3	Clear	B4	
Ċ	100	Clear	C1	Clear	C2	Clear	C3	Clear	C4	
D	100	Clear	D1	Clear	D2	Clear	D3	Clear	D4	
E	100	Clear	E1	Clear	E2	Clear	E3	Clear	E4	
<u>E</u>	100	Clear	E1	Clear	E2	Clear	E3	Clear		

 Table 4.03:
 Evaluation results for Surfactant Sample No. 6-79

Surfactant

: Sample No. 6-66 Polymer : Superfloc BD319

Colution	Quantity			Surfactar	nt @ c	oncentration			PORKU
Solution	ml	0.05%		0.10%		0.15%		0.20%	
A	100	Clear	A1	Clear	A2	Clear	A3	Clear	A4
В	100	Clear	B1	Clear	B2	Clear	B3	Clear	B4
С	100	Clear	C1	Clear	C2	Clear	C3	Clear	C4
D	100	Clear	D1	Clear	D2	Clear	D3	Clear	D4
E .	100	Clear	E1	Clear	E2	Clear	E3	Clear	E4

 Table 4.04:
 Evaluation results for Surfactant Sample No. 6-66

4.1.1 Discussion

Based on the results, the main intention of preparing the surfactant samples is to initially evaluate the reaction with the injected/produced water and to prepare the samples for the IFT and PB experiments. Different surfactant concentrations and injected/produced water would the main attention for the evaluation, and the results from the table have shown positive results for the surfactants analyzed.

Theoretically, for CEOR that is effectively applied for an oil reservoir, the reaction analysis of the surfactant with injection/produced water is crucial so that its reaction does not produce any undesired conflicts whereby precipitations This can be explained by different salinity water conditions would occur. imposed by various oil reservoirs worldwide. In reality, the chemical compositions of the injection/produced water of an oil reservoir are not similar to other oil reservoir due to different geographical positions. For instance, the salinity content of an oil reservoir in Malaysia is different compared to oil reservoirs in Canada and the Middle East. Most of oil reservoirs in Malaysia possess high salinity content compared other oil reservoirs, and therefore a specific CEOR must be design in order to tolerate the salinity content and at the same time maintains recovery efficiency. This explains why various surfactants from different manufacturers are taken for fluid-fluid evaluation testing, so that it would comply with the chemical nature of the injection/produced water.

The desired results of the reaction of the surfactants and the injection/produced water can be indicated from physical observation, where no precipitation would occur and the solution is in clear condition. From the tabulated results of surfactant samples, all the samples from different surfactant concentrations have shown clear conditions after it is mixed with the injection/produced water and the

crude oil. Thus, at this point, it can be concluded that the surfactants analyzed complies with the nature of the specific oil reservoir.

Figure 4.01: Surfactant Sample Results for Sample no. 6-79

Figure 4.02: Undesired Surfactant Reaction with Injection/Produced Water

4.2 Determination of Interfacial Tension (IFT) of Surfactants 6-79 and 6-66

The results of determination of IFT of the surfactant samples can be divided to several phases, where elongated oil droplet is measured and recorded, and later it is keyed in the spreadsheet to calculate the IFT values. All the results are referred to Table 4.05 and Table 4.06.

Surfactant	
:	Sample no. 6-79
	Superfloc
Polymer :	BD319

Solution	Density @ 20oC	Density @ 50oC	Rl	R2	R2 - R1	Speed
A1	1.0242	1.0274	9.45	14.27	4.82	17.69
A2	1.0240	1.0045	10.46	14.97	4.51	17.04
A3	1.0238	1.0270	10.55	15.08	4.53	17.01
A4	1.0238	1.0270	7.56	12.82	5.26	17.01
B1	1.0189	0.9994	7.89	14.61	6.72	16.98
B2	1.0188	0.9993	8.56	13.94	5.38	17.03
B3	1.0189	0.9994	8.64	14.70	6.06	16.99
B4	1.0188	0.9993	8.08	14.57	6.49	16.98
C1	1.0138	0.9942	7.87	13.87	6.00	17.01
C2	1.0136	0.9940	9.12	13.79	4.67	17.05
C3	1.0136	0.9940	10.45	15.96	5.51	17.07
C4	1.0136	0.9940	10.36	16.15	5.79	17.02
				· · · · · ·		
D1	1.0090	0.9894	8.26	14.40	6.14	17.01
D2	1.0089	0.9893	10.34	15.87	5.53	16.98
D3	1.0090	0.9894	8.23	13.87	5.64	16.96
D4	1.0090	0.9894	8.25	14.94	6.69	16.95
E1	1.0140	0.9844	7.47	14.84	7.37	16.98
E2	1.0136	0.9838	8.23	13.64	5.41	17.01
E3	1.0136	0.9838	7.44	14.26	6.82	17.05
E4	1.0137	0.9839	7.34	14.38	7.04	17.12

|--|

The densities of the solution samples are calculated using the densitometer. From the results themselves, it can be understood that the density of the sample A to E increases. This can be explained by the variation of injection/produced water compositions among the samples. For the experiments conducted, the parameters in **Table 4.05** are illustrated as follows:

Figure 4.03: Illustrative definitions of R₁ and R₂

The centrifugal speed can be monitored at the rev counter, and its speed can be manipulated by turning the knob at the rev counter. The speed must be recorded for each sample tested in order to calculate the interfacial tension. After the data are recorded, the values are keyed in the spreadsheet to calculate the value of IFT. The equation used is a correlation used in many EOR researches, which is:

IFT = (Spinning Drop Constant) (Speed (ms/rev))⁻² (
$$R_2 - R_1$$
)³ ($\rho_s - \rho_c$)....(4.1)

Where the

Spinning Drop Constant = 0.520 ρ_s = density of solution, (g/cm³) ρ_c = density of crude oil, (g/cm³) = 0.85

Surfactant	
:	SS 6066
	Superfloc
Polymer :	BD319

Solution	Density @ 20oC	Density @ 50oC	R 1	R2	R2 - R1	Speed
A1	1.0239	1.0044	7.37	14.12	6.75	16.96
A2	1.0242	1.0047	7.41	13.77	6.36	17.05
A3	1.0242	1.0047	8.30	14.68	6.38	17.08
A4	1.0241	1.0046	7.11	15.40	8.29	17.02
B1	1.0192	0.9997	5.77	16.84	11.08	17.01
B2	1.0193	0.9998	6.10	16.18	10.08	16.99
B3	1.0194	0.9999	6.40	16.50	10.10	16.99
B4	1.0194	0.9999	6.15	16.69	10.55	16.97
CI	1.0135	0.9939	6.37	15.70	9.33	17.06
C2	1.0137	0.9941	7.13	15.97	8.85	17.02
C3	1.0141	0.9945	7.10	15.76	8.66	17.02
C4	1.0142	0.9946	6.80	15.82	9.02	17.03
D1	1.0082	0.9886	6.91	16.74	9.84	17.05
D2	1.0083	0.9887	7.13	15.58	8.45	17.00
D3	1.0084	0.9888	7.24	15.34	8.11	16.97
D4	1.0083	0.9887	6.74	15.98	9.24	16.95
E1	1.0043	0.9847	5.90	16.46	10.56	17.00
E2	1.0039	0.9843	7.98	17.71	9.74	17.01
E3	1.0040	0.9844	6.25	16.49	10.24	17.07
E4	1.0041	0.9845	5.89	16.73	10.84	17.03

 Table 4.07: Input Results of the Elongated Oil Drop from Spinning Drop Tensiometer

 (6-66)

Similarly, the values of the R_1 and R_2 are placed into the IFT equation in order to calculate the IFT values. Sample calculation of determining IFT can be referred on the next page:

Sample A1:

IFT = (Spinning Drop Constant) (Speed (ms/rev))⁻² ($R_2 - R_1$)³ ($\rho_s - \rho_c$)....(4.1)

= $0.520 \text{ x} (16.96 \text{ ms/rev})^{-2} \text{ x} (14.12 - 7.37)^3 \text{ x} (1.044 - 0.85 \text{ g/cm}^3)$

= 0.086

The remaining results for the rest of the samples are tabulated below:

Injection Water	Produced Water	Interfacial Tension (dynes/cm)*				
wt %	wt %	0.05 wt%	0.10 wt%	0.15 wt%	0.20 wt%	
100.000	0.00	0.086	0.071	0.072	0.158	
75.000	25.00	0.366	0.071	0.072	0.138	
50.000	50.00	0.209	0.179	0.169	0.190	
25.000	75.00	0.236	0.151	0.134	0.198	
0.00	100.00	0.286	0.223	0.258	0.307	

Table 4.08: IFT results for Surfactant Samples (Sample No. 6-66)

Detail calculations for the rest of samples can be referred to the appendices. As for the graphical results, a plot of IFT reduction versus surfactant concentration is illustrated on **Figure 4.05**.

Sample A1:

IFT = (Spinning Drop Constant) (Speed (ms/rev))⁻² ($R_2 - R_1$)³ ($\rho_s - \rho_c$)....(4.1) = 0.520 x (16.96 ms/rev)⁻² x (14.12 - 7.37)³ x (1.044-0.85 g/cm³) = 0.086

The remaining results for the rest of the samples are tabulated below:

Injection Water	Produced Water	Interfacial Tension (dynes/cm)*					
wt %	wt %	0.05 wt%	0.10 wt%	0.15 wt%	0.20 wt%		
100.000	0.00	0.086	0.071	0.072	0.158		
75.000	25.00	0.366	0.277	0.278	0.318		
50.000	50.00	0.209	0.179	0.169	0.190		
25.000	75.00	0.236	0.151	0.134	0.198		
0.00	100.00	0.286	0.223	0.258	0.307		

 Table 4.11:
 IFT results for Surfactant Samples (Sample No. 6-66)

Detail calculations for the rest of samples can be referred to the appendices. As for the graphical results, a plot of IFT reduction versus surfactant concentration is illustrated on **Figure 4.05**.

Figure 4.05: IFT Reduction versus Concentration (Sample No. 6-66)

4.2.1 Discussion

In this experiment, the main target is to selectively identify the sample which has the lowest IFT values. This is generally true because theoretically, the surfactant has the ultimate function to lower the IFT between the crude oil and the water. Thus, the first approach is to determine the IFT using the Spinning Drop Method. This particular method is typically used in determining the IFT due to its simplicity and gives a fairly good estimation. The only equipment used in this experiment is the Spinning Drop Tensiometer, which uses the centrifugal concept to calculate the elongated oil and surfactant droplet. Referring to the results, all the surfactant samples have lowered the IFT between the crude oil and the surfactant solution. In detail, the lowering IFT by the presence of surfactants can be explained in terms of physico-chemical property changes. Initially, without the presence of surfactant, the crude oil is binding with the fluids (water) and the rock due to high interfacial tension. Normally this values ranges from 3-5 dynes/cm (Schramm, 2000) and makes it difficult for normal recovery mechanisms to recover the crude oil. Introduction of surfactants would interrupt the surface tension of the crude oil and the water via dissolved hydrophilic and hydrophobic molecular structures. Consequently, the solvent molecules in the bulk solution (oil and water) interact within similar molecules within the solvent. The surfactant molecules at the interface reduce this force imbalance or surface tension. Previous experimental results show that the presence of surfactants lower the IFT to the range of 0.002 dynes/cm, and this is significantly ideal condition in order to recover more oil and improved oil recovery performance.

For the surfactants analyzed, the IFT lowering performance results showed that surfactant sample 6-79 gives lower range of IFT compared to sample 6-66. However, the IFT lowering results for the samples 6-79 and 6-66 did not reach to the values of 0.002 dynes/cm, but ranges between 0.05 dynes/cm – 0.4 dynes/cm. This means that the minimum and maximum deviations for desired IFT lowering in comparison with the experimental results are:

% deviation = (Results – Desired results)/ Desired Results x 100%

Note: 1 fold = 100%

 $(0.05 - 0.002)/0.002 \times 100\% = 2400\%$ or 24 folds (minimum deviation) $(0.40 - 0.002)/0.002 \times 100\% = 19900\%$ or 199 folds (maximum deviation) Clearly, the deviation values largely deviates from the desired figure based on theory. The minimum deviation from the desired values has folds figure, which is 24 folds. This triggers several possible causes; either the experimental execution errors, or the nature of the surfactant and the water compositions of the selected oil reservoir.

The experimental execution errors could be one of the possibilities that contribute large deviations of the results. During the experiment, there are no certain standards in injecting the amount of surfactant samples into the spinning drop Tensiometer. Different amount of injected samples results different physicochemical reactions to the crude oil, thus they will yield different IFT results. In addition, the spinning drop Tensiometer used does not have a calibration history. Calibration history is important because it would indicate the capability of the equipment producing accurate results. Calibration is particularly important in order to flush and cleanse the impurities left inside the Tensiometer. Unfortunately, the calibration history of the Tensiometer is unavailable and this results ambiguity of the samples injection because of a possibility of previous samples that contaminate the current injection and alters the diameter calculations for the elongated oil and solution droplet. As a consequence, the IFT results have low confidence strength, and the methods of determining the IFT may need to be revised again. Co-currently, the skills of executing the experiments is not refined in order to achieve the desired results. This can be due to the experiments conducted in a pilot scale, where all IFT experiments are done during the first time. As the experiments are classified as qualitative measurements, general errors such as contamination of the samples during injection or filling to the capillary tube occur and results large deviations for IFT determinations. The experiments may need to retested and executed over again so that the consistency and the accuracy of the results can be achieved.

4.3 Phase Behavior (PB) Identification of Surfactant 6-79 and 6-77

The identification of Phase Behavior of surfactant samples 6-79 and 6-66 is achieved after determining the IFT values. The classification results are done by physical observation of the samples that are heated and kept for duration of 2 weeks. Following are the physical observations of the surfactant samples:

Figure 4.06: PB Results for 6-79 Sample A

Figure 4.07: PB Results for 6-79 Sample B

Figure 4.08: PB Results for 6-79 Sample C

Figure 4.09: PB Results for 6-79 Sample D

Figure 4.10: PB Results for 6-79 Sample E

The classification is done based on evaluations on Table 2.01. Results are tabulated on Table 4.12.

.

Surfactant : Sample no. 6-79 Polymer : Superfloc BD319

Colution	Equilibra	ted Phase	Volumes	Phase	Phase	in an
Solution	Bottom	Middle	Тор	Туре	Code	(dyne/cm)
·A1				[] -	LY, C	0.033
A2				-	LY, C	0.025
A3				<u> </u>	LY, C	0.030
A4				łl -	LY, C	0.046
B1	19.0	1.0	50.0	- 111	Y, T	0.082
B2				+	С, Т	0.042
B3	48.0	2.0	50.0	III	LY, C	0.060
B4				-	LY, C	0.074
		i i sedoni kan				
C1				[] +	М	0.056
C2			 	il +	с	0.026
C3				+	М	0.043
C4				+	М	0.050
D1				II -	Y, T	0.058
D2				-	Y, T	0.043
D3				-	Y, T	0.045
D4				-	Y, T	0.076
E1				<u> </u>	В, Т	0.097
E2				-	В, Т	0.038
E3				-	B, M	0.076
E4				11 -	B, M	0.083

B = brown

C = clear

G = grey

M = milky
W = white
Y = yellow
L = light
D = dark
T = translucent
O = opaque
PPT = precipitate
Table 4.12: PB Classification for Surfactant Sample 6-79

For surfactant sample 6-66, the results are similarly presented as compared to sample 6-79. The results are shown in the following:

Figure 4.11: PB Results for 6-66 Sample A

Figure 4.12: PB Results for 6-66 Sample B

L = light D = dark T = translucent O = opaque PPT = precipitate Table 4.10: PB Results Classifications for 6-66 surfactant samples

4.3.1 Discussion and Recommendation

For experiment involving phase behavior, the strategy is to classify the samples in terms of types. As explained in theory, the desired phase behavior of a good surfactant is to have phase type III, where three or more fluid envelopes exist, which comprises of bottom aqueous phase, middle emulsion phases, and top crude oil phase. This can be done via physical observation, and later it is tabulated so that the performance of the samples can be viewed in overall. The fundamental concept of having the phase behavior analysis is to provide the interaction of surfactants with the oil and water so that an effective flooding design can be designated to meet the specific reservoir conditions for CEOR. Ranking performance of the following phase behavior types are type II-, type II, and type II+.

Based on the results, it can be said that most of the samples are type II- for surfactant 6-79 and 6-66. Results for type III and type II+ is tabulated below:

Туре	Surfactant				
	6-79	6-66			
III .	B1,B3	B1,B2,B3			
II+	B2,C1,C3,C4	A1,A2,A3,A4			

 Table 4.11:
 Performance Division of Phase Behavior Results

The tabulated results for the PB classification can be referred below:

Surfactant SS : 6066 Polymer : Superfloc BD319

	Equilibrated Phase Volumes %			Phase	Phase	IFT
Solution	Bottom	Middle	Тор	Туре	Code	(dyne/cm)
A1				+	С, Т	0.086
A2				+	С, Т	0.071
A3				+	С, Т	0.072
A4		IN THE R. LEWIS CO.		+	С, Т	0.158
B1	50.0	0.5	49.5	- 111	С, Т	0.366
B2	49.0	1.0	50.0	III	С, Т	0.277
B3	47.0	3.0	50.0	- III	М, Т	0.278
B4			the second s	11 -	LY, T	0.318
C1				-	P, Y	0.209
C2				11 -	Ρ, Υ	0.179
C3] -	Ү, Т	0.169
C3				-	P, Y	0.190
						good graat and a
D1				-	В	0.236
D2		-		II -	P, B	0.151
D3				<u> </u>	P, B	0.134
D4				-	В	0.198
			0.000.000			
E1				II -	DB, T	0.286
E2				<u> </u> -	DB, T	0.223
E3				11 -	DB, T	0.258
E4				11 -	DB, T	0.307

B = brown

C = clear

G = grey

M = milky

W = white

Y = yellow

L = light

D = dark

T = translucent

O = opaque

PPT = precipitate

 Table 4.13:
 PB Results Classifications for 6-66 surfactant samples

4.3.1 Discussion and Recommendation

For experiment involving phase behavior, the strategy is to classify the samples in terms of types. As explained in theory, the desired phase behavior of a good surfactant is to have phase type III, where three or more fluid envelopes exist, which comprises of bottom aqueous phase, middle emulsion phases, and top crude oil phase. This can be done via physical observation, and later it is tabulated so that the performance of the samples can be viewed in overall. The fundamental concept of having the phase behavior analysis is to provide the interaction of surfactants with the oil and water so that an effective flooding design can be designated to meet the specific reservoir conditions for CEOR. Ranking performance of the following phase behavior types are type II-, type II, and type II+.

Based on the results, it can be said that most of the samples are type II- for surfactant 6-79 and 6-66. Results for type III and type II+ is tabulated below:

Туре	Surfactant			
	6-79	6-66		
III	B1,B3	B1,B2,B3		
II+	B2,C1,C3,C4	A1,A2,A3,A4		

 Table 4.14:
 Performance Division of Phase Behavior Results

From Table 4.14, there are two samples managed from type III for surfactant 6-79, while for three samples for surfactant 6-66. These samples are considered the ideal samples that satisfy the desired phase type. Unlike type II+, the samples gathered are likely to be retested and may subject to short listing.

The significance having type III Phase Behavior is to provide clear distinction of all three fluid phases. In a chemical flooding design, the goal is to minimize the chemical reaction between the oil and the surfactant, while at the same time maintains its recovery performance by lowering the IFT and maximizing mobility control by usage of polymer solution. By having phase type III, less oil is solubilized in a form of emulsion and this is important when the oil is transported to the production tube and undergoes refining process. Logically, by presence of emulsions, it makes separation of oil, water, and surfactant difficult because the goal is to recover back the surfactant that is to be reused again in CEOR. As surfactants are highly expensive chemicals, most flooding designs aim to minimize the surfactant losses; so that the chemical treatment still maintains economic viability of the CEOR.

One of constraints faced in phase behavior discussion is its complex chemistry fundamentals. In detail, the true compositions of the reservoir are heterogeneous, and the fluids within the reservoir do not behave as absolute true components. Phase diagram is one alternative to describe the phase behavior of the reservoir oil, but the explanation is merely an estimate and may subject to several ambiguities. The only option to study the phase behavior is to continuously conducting experiments, so that more information regarding the surfactant's nature in phase behavior can be extracted. This complex chemistry can only be done with the collaboration with highly expert chemists and reservoir engineers, which is specialized in EOR processes.

The experiment conducted involving phase behavior is done in a pilot scale, where the experiments are done for the first time. Thus, the results gathered during the experiment may deviate from true results, and one of the best options in order to improve the experimental results is to redo the experiments so that the accuracy and the consistency can be achieved. As phase behavior classification is done by physical observation, this type of method is subjective, and the classification results may differ due to different kinds of interpretation. The alternative to compensate this ambiguity is to conduct together along with other EOR chemists or reservoir engineers, so that the observation results agree with one sample to another.

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conjunction with the research objectives, EOR is a valuable area of research because of its potential to further recover more oil. Due to its increasing challenges faced by the petroleum industry, EOR has been the priority and it is up to the engineers to develop and improve recovery techniques in order to design an effective recovery mechanism. Chemical flooding is one of the EOR mechanisms that apply the usage of surfactants to recover more oil. Its capability to lower the interfacial tension between the crude oil, water and rock due to its hydrocarbon and hydrophilic structure has become the major interest of research and studies about its physical chemistry so that its properties can be very well understood. One of the properties that it is studied in this research is the IFT and Phase Behavior determination of the selected samples, specifically surfactant 6-79 and 6-66. These are done by conducting experimental works, and three experiments are conducted at PRSS, Bangi. Analysis of the experimental results are also discussed together along with the EOR Chemist and the Petroleum Engineer and based on analysis of the surfactants, the results gathered are satisfactory and most of the samples converge to the desired results. For the IFT experiments, the determination is done by the Spinning Drop Method, and the IFT results gathered are within 0.02 - 0.4 dynes/cm, and at this moment, surfactant sample 6-79 gives best lowering IFT results. As for PB identification, most of the samples yield type II-, a fair desirable results, and a few of samples managed to obtain type III.

5.2 **Recommendations**

To improve the quality of this research, the experiments must be repeated for a number of times so that the consistency and the accuracy of the results can be achieved. As this research environment involves a lot of qualitative experimental works, errors are mostly evident and this disrupts the results' accuracy and consistency. This can be resolved by improving the experimental methods, by revising the methods used, and if possible, other experimental methods can be used so that the results of the alternative method agree with the current methods and strengthens the results credibility. Plus, the equipments used must be at its optimum condition with good calibration history so that the results calculated are accurate and consistent.

Since this research project involves analysis of the fluid-fluid evaluation of the surfactants, it is recommended that this research be continued by future research so that the study of surfactant properties can be intensified. As this project plays a huge impact to the development of CEOR, this research is proved valuable in terms of economic impact to oil industries in the race of recovering more oil.

CHAPTER 6 REFERENCES

- 1. Laurier L. Schramm, 2000, Surfactants: Fundamental and Applications in the Petroleum Industry, Cambridge; Cambridge University Press
- 2. Donaldson, Chilingarian, Yen, 1983, Enhanced Oil Recovery Volume I: Fundamentals and Analyses, Elsevier
- 3. K.R. Lange, 1999, Surfactants: A Practical Handbook, Hanser Publications
- 4. Bradly, 1987, Petroleum Engineers Handbook, Society of Petroleum Engineers
- 5. Thomas M. Schmitt, 1992, Analysis of Surfactants, MDI Publications
- 6. D.R. Karsa, 1998, New Products and Applications in Surfactant Technology, CRC Publications
- 7. The Petroleum Geology and Resources of Malaysia, Petronas

APPENDICES

Related Figures

Figure 7.01: Chemical Flooding Design

Figure 7.02: Interior of the oven

Figure 7.03: Experimental Work Platform